

Bentazone Leaching in Spanish Soils

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Abstract: Adsorption, incubation and soil-column experiments with bentazone [3-isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide] were carried out in ten different soils from the marches surrounding the Doñana National Park (Huelva, SW Spain). Adsorption isotherms for the different soils showed a good fit with the Freundlich equation. Bentazone was poorly adsorbed in all the soils studied, with no significant relationship between the K_f values and soil characteristics. A significant correlation was obtained between the soil organic matter content and the distribution constant values (K_d) calculated at an equilibrium concentration of $200 \mu\text{g cm}^{-3}$. The low adsorption and non-degradation of bentazone on these soils suggest that the herbicide readily percolates through soils to reach the surface and ground waters. The mobility of bentazone through three soil columns was also studied. The mass balances carried out showed that bentazone was totally eluted from the soil columns. The theoretical model applied to explain bentazone leaching under our experimental conditions seems to be suitable for soil columns with a uniform water-flow rate.

Keywords: adsorption, soil columns, leaching, bentazone, herbicides.

1 INTRODUCTION

Bentazone is a herbicide used to treat broad-leaf weeds in a variety of crops. As a consequence of its widespread use, bentazone residue levels of about $1.0 \mu\text{g dm}^{-3}$ have been detected in deep ground water in western Europe.¹ This, in turn, agrees with the findings of authors² who investigated the soil-column mobility of bentazone and found that 74–97% of it is eluted. However, in lysimeter studies by other authors,^{3–5} less than 2% of the bentazone applied to soil was eluted, while about 50% was lost as a result of volatilization and/or mineralization.⁶ These apparently conflicting results might have been due to differences in the experimental techniques used as well as in the soil properties, which could produce different water-flow rates in the soils.

The aim of the present paper was to study the adsorption and degradation of bentazone in different soils sampled from the marches surrounding the Doñana National Park, Huelva (SW Spain). Awareness of pollution hazards will be a key factor in the future effective management of this important nature reserve. As the agro-industrial activities carried out in the area

could play a significant role in pollution, leaching experiments with soil columns were also carried out. The leaching of bentazone through soil columns was simulated with a theoretical model based on one-dimensional transport, a steady water-flow rate and an instantaneous adsorption–desorption equilibrium.

2 MATERIALS AND METHODS

2.1 Materials

Ten soils from the Doñana National Park (Huelva, SW Spain) were studied. Their properties are shown in Table 1. The samples were taken from the A-horizon and passed through a 2-mm sieve. pH was determined from slurries with a soil–water ratio of 1:2 by mass. Organic matter was analysed by the method described by Walkley and Black,⁷ and clay minerals by X-ray diffraction. Mechanical analysis and CEC were measured following the 3A1 and 5A1 methods, respectively, of the Soil Conservation Service.⁸

TABLE 1
Soil Properties

Soil	Subgroup	pH	Sand (%)	Silt (%)	Clay (%)	O.M. (g kg^{-1})	CEC (cmol kg^{-1})	Phyllosilicates (%) ^a	Smectite (%) ^a
P ₁	Xerofluvent	8.17	26.3	21.9	51.8	22.3	24.7	37	20
P ₂	Typic Rodoxeralfs	7.99	73.0	3.3	23.7	10.8	8.8	25	14
P ₃	Xerofluvent	7.69	11.2	26.7	62.1	13.1	21.4	47	30
P ₄	Mollic Haploxeralf	7.94	74.9	8.4	16.7	6.1	9.0	21	12
P ₅	Chromoxerert	7.96	32.0	14.3	52.7	14.5	27.9	44	38
P ₇	Entic Pelloxererts	7.70	13.4	24.0	62.6	24.5	28.8	52	18
P ₈	Typic Chromoxerert	8.02	59.6	12.3	28.1	17.4	13.3	37	18
P ₉	Palixeralf	5.54	78.9	6.6	14.5	11.0	3.5	23	6
P ₁₀	Salorthidic Fluvaquent	8.13	4.3	52.9	42.8	5.2	24.2	77	39
P ₁₁	Fragixeralf	7.48	68.2	6.6	25.2	4.5	14.5	31	26

^a Percentage in the total soil.

2.1.1 Organic compounds

Bentazone, as an analytical standard of known purity (99.5%), was supplied by BASF (Limburgerhof, Germany). Its solubility in water, at 20°C, is about 500 mg dm³. Acetone and methanol for HPLC were obtained from Panreac (Madrid, Spain).

2.2 Adsorption measurements

The adsorption of bentazone at 15°C was measured in duplicate samples of the ten soils. Four bentazone solutions (300, 200, 100, and 50 mg dm⁻³) in distilled water were used. Aliquots (20 cm³) of the four bentazone solutions were added to soil (4.00 g) in 50-cm³ tubes. The tubes were mechanically shaken (end-over-end) for 24 h in a thermostatic chamber (kinetic experiments indicated that the adsorption of bentazone by the soil samples had reached an apparent equilibrium after 4 h). The suspensions were then centrifuged at 1720g for 20 min, and bentazone was measured in the supernatant phase by HPLC, as describe below.

2.3 Incubation experiments

Soil incubation experiments were carried out to measure the rate of bentazone disappearance in two representative soils P₂ (sandy clay loam) and P₇ (clay).

The soil samples, stored in closed plastic bags under laboratory conditions, were mixed, and portions equivalent to 20 g of dry soil were weighted into 250-cm³ glass bottles. For each soil, two series of ten bottles were moistened with water (3 cm³) and preincubated for three days in a thermostatic chamber at 20(±1)°C. Aliquots (4 cm³) from a bentazone solution in water (268 mg dm⁻³) were dripped with a syringe onto the soils in the bottles as homogeneously as possible. The contents of the bottles were mixed, partially covered with aluminium foil to maintain aerobic conditions, and

placed in a dark thermostatic chamber at 20(±1)°C, where a water-saturated atmosphere prevented the soil samples from drying out. The moisture contents of two further samples of each soil were determined at 105°C; values of 72% and 100% were obtained for the field capacity of the P₂ and P₇ soils, respectively. After incubation periods of 0, 1, 3, 7, 14, 28, and 35 days, one bottle of each series was frozen at -15°C to stop degradation. Finally, the samples were defrosted and extracted for subsequent liquid chromatography analysis.

2.4 Extraction method

Two extraction methods were compared in order to evaluate their efficiency in the extraction of bentazone from soils. For both methods, aliquote (4 cm³) of the standard bentazone solution were added to three replicated soil samples.

For the first method, the soil samples were extracted by shaking with methanol for 8 h. After three extractions and centrifugations, the supernatants were collected together, evaporated to 2.5 cm³ under vacuum at 65°C and then chromatographed.

For the second method, the soil samples were extracted by soxhlet with methanol (50 cm³) at 90°C for approximately 8 h. The total extract was evaporated to 2.5 cm³ under vacuum at 65°C and then chromatographed.

The bentazone recoveries were 63.8(±10.6)% and 100.1(±6.5)% for the first and second methods, respectively. The soxhlet method was thus judged to be the more efficient.

2.5 Leaching experiments with soil columns

The leaching of bentazone in soil columns was studied with three consecutive soils of contrasting texture, i.e. P₂ (sandy clay loam), P₇ (clay), and P₁₀ (silty clay).

The columns used were polyacrylate cylinders (0.3 cm walls; 9.3 cm ID \times 20 cm long) with an outlet tube at the bottom for collection of the percolation water. Column packing was carried out by first filling the cylinders with a sand filter (5 cm thick), to facilitate the flow of water from the columns. The washed sand was graded, from coarse (about 2 mm) at the bottom to fine (about 0.2 mm) at the top. The cylinders were then filled with a layer (10 cm) of dry soil and, finally, a top layer (1 cm) of coarse sand.

A rainfall simulator, fed with water from a variable peristaltic pump (model VL: Autoclude, UK), was placed on top of the cylinders. The leaching experiment started after a few days of percolation, when a steady-state flow rate was achieved in the column. Aqueous calcium chloride (0.1M; 50 cm³) was dripped uniformly onto the column. Chloride ion was used as a tracer to characterize the water-flow rate in the soil columns. The irrigation period in the P₁₀ soil column, which showed a slower flow rate than the P₇ and P₂ soil columns, was 35 cm³ day⁻¹ for 30 days whereas the P₇ and P₂ soil columns, with similar flow rates, were irrigated with the rainfall simulator at 67(\pm 5 cm³ h⁻¹) for three days (8 h per day). The leachates from these columns, collected daily (P₁₀), hourly or half-hourly (P₇ and P₂), were stored at 4°C before analysis. When the chloride ion had been totally eluted from the columns, bentazone in water (10 cm³) was dripped uniformly onto the soil columns (P₂, P₇ and P₁₀). The total amounts of bentazone applied were 3.1 mg for P₁₀, and 4.79 mg for P₂ and P₇ (i.e. four and seven times the recommended amounts, respectively). The leachates from these columns were collected and stored in the same way as that described for the chloride-ion tracer, before liquid chromatography analysis.

At the end of the leaching experiment, the soil columns were divided into soil layers (about 3 cm), and the mass of wet soil per layer was determined. Two subsamples of each layer were extracted for 8 h in a soxhlet with methanol (75 cm³).

The soil bulk density (ρ) and soil water content (θ) were determined by the loss of weight of the wet soil samples when dried at 105°C.

The retardation factor of the bentazone was determined from the distribution curve for both the tracer and the pesticide:

$$R = \frac{T_p}{t_i} \quad (1)$$

where R is the retardation factor, and t_p and t_i are the time elapsed until the concentration of pesticide and tracer in the effluent is 50% of the input concentration.

The through transport of water-tracer chloride ion in the soil columns was simulated with a computed model based on the PESTLA model,⁹ with various simplifications such as the non-adsorption and non-transformation of the chloride ion throughout the soil column, and a steady-state water flow at constant soil water contents. The diffusion coefficient of chloride in water (D_0) has been estimated to be 2.8 cm² h⁻¹.¹⁰ The characteristics of the leaching experiment (Table 2) were introduced into the computations, together with the adsorption and degradation constant values calculated in the laboratory.

The experimental movement of bentazone through the soil columns was compared with the average movement expected on the basis of the adsorption coefficients according to the equation:

$$Z_a = \frac{V_e}{\varepsilon_1 + \rho_b K_f} \quad (2)$$

where Z_a is the average distance of movement (cm), V_e the water layer of effluent (cm), ε_1 the volume fraction of the water phase (cm³ cm⁻³), ρ_b the soil bulk density (g cm⁻³), and K_f the adsorption coefficient (cm³ g⁻¹) at an equilibrium concentration of 1 mg dm⁻³.

2.6 Chemical analysis

The bentazone, from water samples and extracted with methanol from soil, was analysed by liquid chromatography.¹¹ The chromatographic conditions were: mobile phase, methanol + 25mM aqueous potassium dihydrogen

TABLE 2
Characteristics of Leaching Experiments with P₁₀, P₇ and P₂ Soil Columns

Soil column	P ₁₀	P ₇	P ₂
Column length (cm)	10	9.5	9.5
Surface area (cm ²)	67.93	67.93	67.93
Soil bulk density (g cm ⁻³)	1.086	0.965	1.276
Volume fraction of water (cm ³ cm ⁻³)	0.58	0.47	0.52
Water flux density	0.529	0.907	0.953
	(cm ³ cm ⁻² day ⁻¹)	(cm ³ cm ⁻² h ⁻¹)	(cm ³ cm ⁻² h ⁻¹)
Total irrigation (cm ³ cm ⁻²)	16.49	20.85	22.87

phosphate (20 + 80 by volume); flow rate, 0.3 ml min^{-1} ; column temperature, 40°C ; detection wavelengths, 225 and 245 nm (bandwidth 4 nm); reference wavelength, 550 nm (bandwidth 50 nm); injection volume, $2 \mu\text{l}$. The detection limit of bentazone, equivalent to $2 \mu\text{l}$ of a solution at a concentration of 0.06 mg dm^{-3} , were 0.12 ng .

The chloride-ion concentration in the soil-column eluates was measured with aqueous silver nitrate (0.1M), using a selective chloride electrode and a pH/mV meter (CRISON).

3 RESULTS AND DISCUSSION

3.1 Adsorption isotherms

The empirical Freundlich relationship was used to describe the results of the bentazone adsorption on soil. The linear form of this equation is as follows:

$$\log x = \log K_f + \frac{1}{n} \log C_e$$

where x is the amount ($\mu\text{g g}^{-1}$) of pesticide adsorbed, C_e the pesticide concentration in the solution at equilibrium ($\mu\text{g cm}^{-3}$), K_f the quantity of pesticide adsorbed when the equilibrium concentration equals one, and $1/n$ reflects the degree of linearity of the adsorption trend. Figure 1 shows the linear isotherms of bentazone adsorption on the ten soils studied. The K_f , $1/n$ and correlation coefficient (r) values are shown in Table 3, together with the distribution coefficients K_d (x/C_e) at an equilibrium concentration of $200 \mu\text{g cm}^{-3}$.

The $1/n$ values for bentazone adsorption on P_2 , P_3 , P_4 , P_7 , P_8 and P_{11} soils were <1 , indicating isotherms which are convex, i.e. of the L type in the Giles classification.¹² The isotherm slope decreases steadily as the solute concentrations increase, since vacant sites become less accessible as the soil surface becomes progressively covered. The curvilinear isotherms suggest that the number of sites available for adsorption becomes a limiting factor.

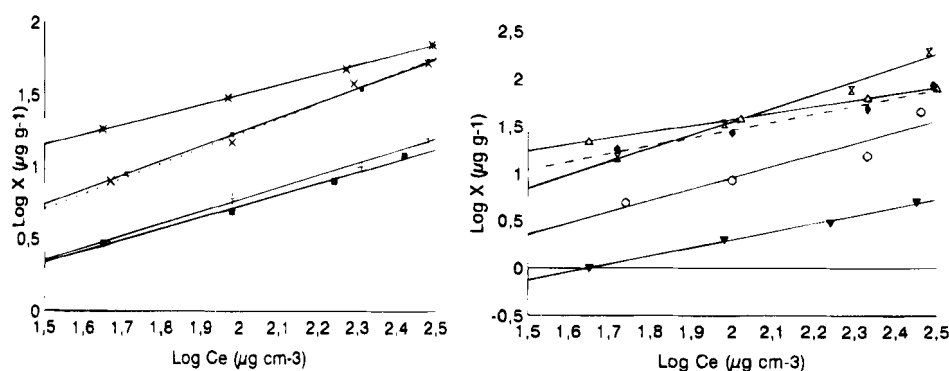


Fig. 1. Adsorption isotherms of bentazone on ten soils at 15°C . (□) P1 (+) P2 (* P3 (■) P4 (x P5 (◆) P7 (△) P8 (⊗) P9 (●) P10 (▽) P11

TABLE 3
Freundlich Constants (K_f and $1/n$) and Correlation Coefficients (r) for the Adsorption of Bentazone on Soils

Soil	$K_f (\text{cm}^3 \text{g}^{-1})$	$1/n$	r^a	$K_d (\text{cm}^3 \text{g}^{-1})^b$
P ₁	0.160	1.02	0.999***	0.178
P ₂	0.120	0.85	0.996***	0.054
P ₃	1.096	0.70	0.987**	0.228
P ₄	0.150	0.77	0.998***	0.044
P ₅	0.131	1.06	0.991***	0.180
P ₇	0.583	0.85	0.986**	0.263
P ₈	1.227	0.69	0.992***	0.232
P ₉	0.050	1.42	0.985**	0.462
P ₁₀	0.035	1.20	0.940*	0.101
P ₁₁	0.039	0.85	0.991***	0.018

^a *** $P < 0.001$; ** $P < 0.01$; * $P < 0.05$

^b K_d is calculated at $C_e = 200 \mu\text{g cm}^{-3}$.

The P_1 and P_5 soils, with $1/n$ values close to 1, gave linear isotherms.

The $1/n$ values for P_{10} and, in particular, P_9 were >1 , giving concave isotherms (i.e. S type in the Giles classification). At low equilibrium concentrations, bentazone was very poorly adsorbed on these two soils. As C_e values increased, there was a significant corresponding increase in the amount of bentazone adsorbed on the P_9 soil. This concentration dependence of the adsorption of bentazone mainly on the P_9 soil could be explained by the nature of this soil. As bentazone is a weak acid ($\text{pK}_a = 3.2$), at a pH below the pK_a it will mainly be in a molecular state. The P_9 soil, with a pH of 5.5, is rich in montmorillonite, a mineral whose surface is highly acidic owing to the hydrolysis of the exchange cations. It was therefore to be expected that bentazone molecules situated on or near these surfaces should be in a molecular state and so be adsorbed by physical forces. This phenomenon will be even more significant at higher bentazone concentrations, where it may break the energy barrier bonding the silicate laminae by the exchange cations, and so penetrate the interlaminar surfaces, thus increasing adsorption.

The K_f values (Table 1) show that the adsorption capacity of bentazone is arranged as follows: $P_8 > P_3 > P_7 > P_1 > P_4 > P_5 > P_2 > P_9 > P_{11} > P_{10}$. Nevertheless, no significant relationship was found between the K_f values and the soil characteristics (Table 1).

No significant correlation was found between the K_d values at an equilibrium concentration of $200 \mu\text{g cm}^{-3}$ (Table 3), and the soil characteristics (Table 1).

As mentioned above, the P_9 soil, owing to its pH value, could have an adsorption mechanism which is different from that of the other nine soils. Thus, by excluding the P_9 soil, a significant correlation between the soil characteristics of the remaining soils and the corresponding K_f or K_d values might be obtained. The correlation results do indeed reveal a relationship between the K_d values and the soil organic matter content, with a correlation coefficient of 0.88^{**} ($P < 0.01$). This is in good agreement with the findings of other authors,² who found that the mobility of bentazone decreases in soils which are rich in organic matter, owing to the adsorption of the pesticide. However, in the present study, no significant relationship was found between the K_f values (the adsorbed quantity at low equilibrium concentration) and the soil organic matter content. Consequently, the organic matter content seems—at least at high equilibrium concentrations—to be the main soil characteristic responsible for the adsorption of bentazone on the soils studied. At low concentrations, the bentazone molecules may be adsorbed onto pores or hydrophobic soil sites. Nevertheless, when the K_f or K_d values obtained are considered, it is clear that the amount of bentazone adsorbed on such soils is very low, suggesting that bentazone moves easily through such soils and is able to reach surface and ground waters.

3.2 Incubation results

Figure 2 shows the results of the soil incubation experiments. The plot of the remaining percentage against time shows that the initial amount of bentazone remained virtually constant in the P_7 soil samples after an incubation period of 30 days. The incubation results for the P_2 samples show that the added amount of bentazone remained constant for the first few days of incubation. Later, there was a slight decrease and the amount of bentazone remaining after 28 days was about 20% less than the initial amount. This again remained stable for the final two weeks of incubation. In the P_7 soil, with higher organic matter content, there was no significant conversion of bentazone after 20 days of incubation. These results would suggest that the adsorption of bentazone by organic matter in the soil protects this pesticide from degradation. Thus, bentazone may have been retained in the P_7 soil, with a high

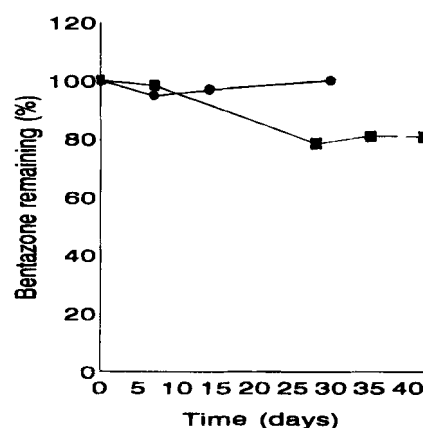


Fig. 2. Disappearance of bentazone at 20°C from (●) P_7 and (■) P_2 soil samples under aerobic conditions.

organic matter content, so partially avoiding its degradation by the micro-organisms present in the soil. A greater degradation of bentazone by the micro-organisms of the soil would be expected in the P_2 soil, with a lower organic matter content. As the leaching experiment was carried out with shorter times (a few hours or days), these results gave a transformation-rate coefficient in the simulation which was effectively zero. However, it is likely that the degradation rate of bentazone under field conditions may be somewhat greater in these soils.

3.3 Column leaching results

3.3.1 Chloride-ion tracer

The chloride-ion concentrations in the leachates from the P_{10} , P_2 and P_7 soil columns, together with the theoretical curves calculated by the model, are shown in Fig. 3.

In the P_{10} soil column, the chloride ion leached through the soil, showing high concentrations in the first eluates. The maximum concentration appeared after eight days, after which there was a sharp decrease in the concentration, which started to flatten out towards the end of the curve.

The results of the chloride-ion tracer leaching simulation with a dispersion distance of $L_{dis} = 2$ cm provided a fairly satisfactory prediction of the experimental data, except for the first few days, when the chloride concentrations measured were higher than those computed. This higher chloride-ion concentration in the effluents indicates that a fraction of the water phase flowed at a faster rate than that corresponding to uniform water flow through the soil column. Given the lack of structure in these sieved-soil columns and the uniform particle size of this silty clay soil (Table 1), and thus a uniform pore-size distribution, it may be that the preferential flow of this water fraction mainly occurs over the wall of the soil column.

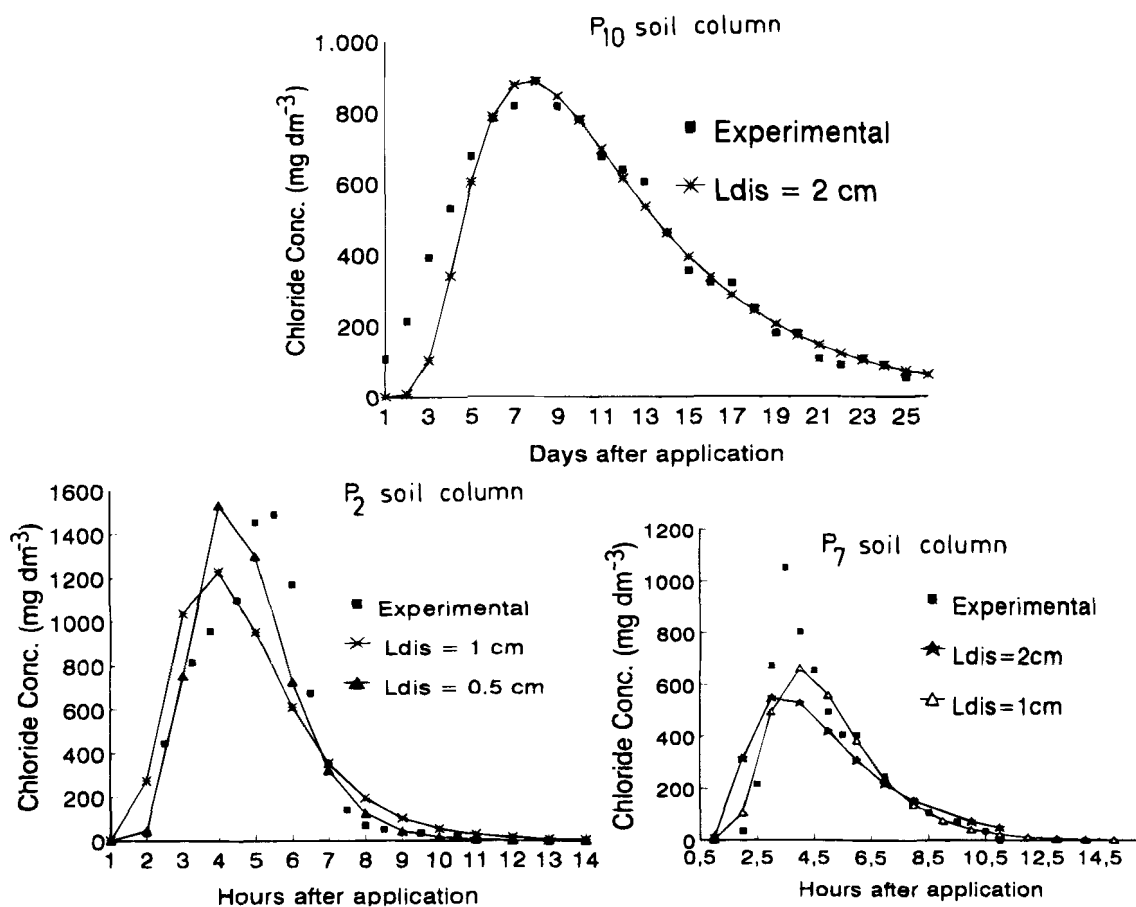


Fig. 3. Experimental data and simulated curves for the leaching of the tracer, chloride ion, in the P_{10} , P_2 and P_7 soil columns.

In the P_2 (sandy clay loam) soil column, the water-flow rate was faster than in the P_{10} column, possibly owing to its lower smectite content and higher sand content (see Table 1). In this soil column, the tracer appeared in the leachate 2 h after it was applied, reaching its maximum concentration after 5.5 h.

The theoretical curves simulated for the leaching of the chloride ion in the P_2 soil column, with L_{dis} values of 0.5 cm and 1.0 cm, do not coincide with the experimental results. In both cases, the maximum appeared 4 h after application, i.e. 1.5 h earlier than the maximum described by the experimental data. Nevertheless, the theoretical curve simulated with an L_{dis} value of 0.5 cm did match the experimental data at both the beginning and the end of the curve. The experimental data peak delay may be due to an anion exclusion process previously described in the flow of anionic tracers in soil columns under similar laboratory conditions.^{13–15}

The P_7 soil column, with a similar irrigation rate to the P_2 soil column ($67(\pm 5) \text{ cm}^3 \text{ h}^{-1}$), also showed similar flow characteristics (Table 2). It should be reasonable to expect that the shape and symmetry of the leaching curve described by the chloride-ion data in both columns would also be analogous. However, displacement of the tracer was faster in the P_7 soil column

than in the P_2 column, appearing in the leachate within the first half-hour and reaching its peak concentration after 3 h. The rapid elution and asymmetric curve may be related to the clay content of the P_7 soil. These minerals show superficial negative charges, which may produce the repulsion of the anionic tracer (Cl^-), and so accelerate its displacement.¹⁶ Thus, the water volume of irrigation for the anion movement may be somewhat lower than the total pore volume of the P_7 soil column.

The simulation leaching curve of the tracer in the P_7 soil column, with an L_{dis} value of 1 cm, gave a better description of the experimental data than the curve simulated with $L_{dis} = 2$ cm. However, the experimental data peak was higher than the simulated one. As mentioned above, this may be due to the anion repulsion of the tracer. This phenomenon was not built into the model.

3.3.2 Bentazone leaching

The bentazone concentrations in the leachates from the P_{10} , P_2 and P_7 soil columns are shown in Fig. 4, together with the theoretical curves calculated by the model, considering the Freundlich adsorption constants

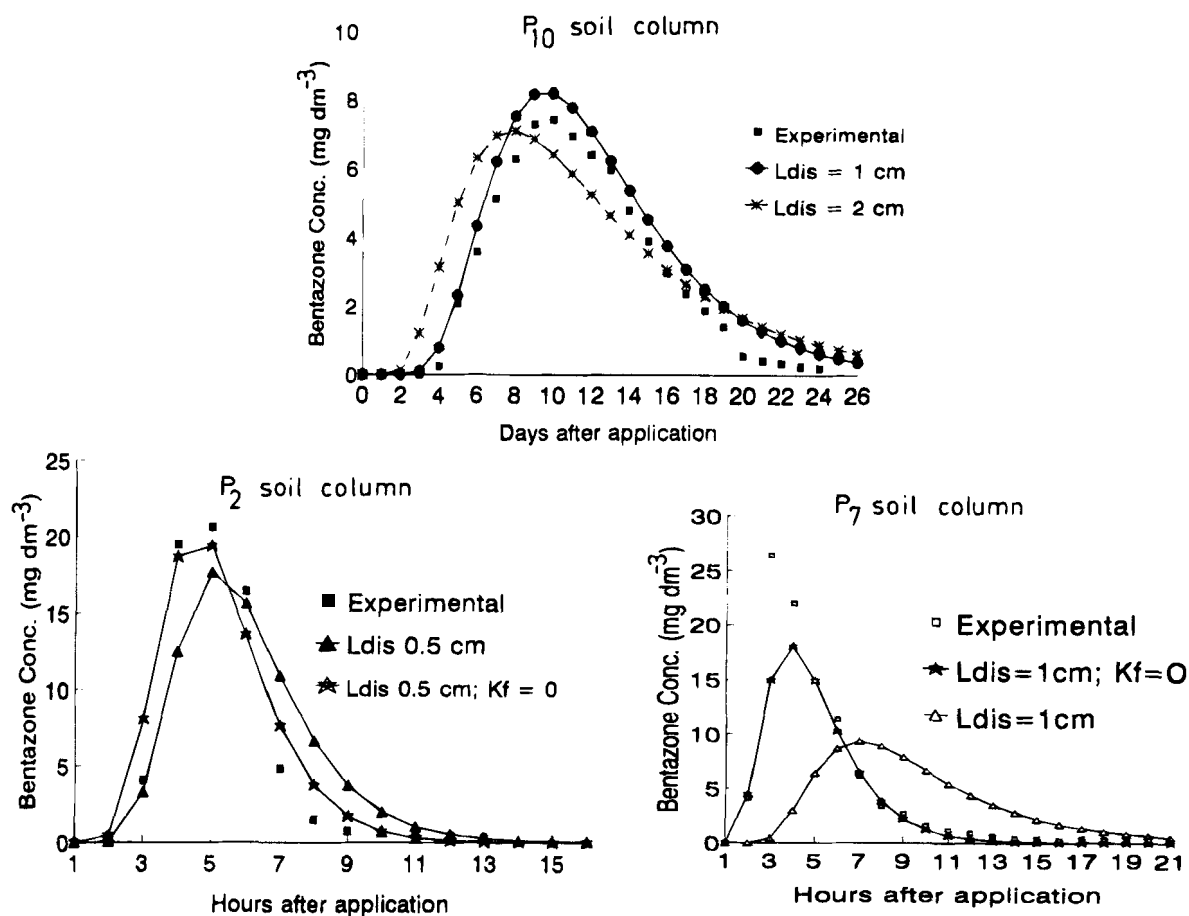


Fig. 4. Experimental data and simulated curves for the leaching of bentazone in the P_{10} , P_2 and P_7 soil columns.

calculated in the laboratory and the dispersion distance value (L_{dis}) which matched the experimental data curve given by the tracer in each column.

In the P_{10} soil column, the bentazone leached through the column more slowly than the tracer, appearing in the eluates two days after application and reaching its maximum concentration in the eluate collected after ten days of irrigation (i.e. two days later than the tracer). This may be due to the adsorption of bentazone in the soil column, or the ease of its flow being impeded by the large size of bentazone molecules.

The bentazone leaching simulation curve in the P_{10} soil column, with $L_{dis} = 2$ cm (i.e. the value obtained from the tracer fitting curves) gave a poor description of the experimental leaching of bentazone in this soil. The best description was given by the curve with $L_{dis} = 1$ cm, which reached its peak concentration at the same time as the experimental data, albeit with slightly higher concentrations. Other authors¹⁷ have suggested that such minor anomalies may be due to differences between the amounts of bentazone adsorbed in the batch and soil-column experiments.

The experimental data curve of bentazone does not match the theoretical curve with the same dispersion distance as the tracer, perhaps because the elution of the tracer and pesticide is staggered rather than simulta-

neous. With increasing elution time, small soil aggregates may be modified, leaching to more homogeneous porosity and thus a lower dispersion in the flow of the solute through the soil column. This phenomenon of aggregation is expected if one considers the smectite content of this soil, which may form highly stable aggregates with the organic matter.

The retardation factor calculated with eqn. (1) for bentazone displacement in the P_{10} soil column was 1.33. Such a small value suggests that bentazone is a very mobile herbicide in this type of soil, and agrees with the average displacement distance estimated by eqn (2) (i.e. 26.68 cm—about twice the length of the soil column). This theoretical displacement also agrees with experimental results. The mass balance shows that more than 88% of the initial amount of bentazone applied was present in the leachate, while only 1% remained in the column after irrigation with distilled water ($16.49 \text{ cm}^3 \text{ cm}^{-2}$).

In the P_2 soil column, bentazone appeared in the water percolated 3 h after irrigation began (1 h later than the tracer), reaching its peak concentration after 5.5 h.

The simulation leaching curve for bentazone in the P_2 soil column, with $L_{dis} = 0.5$ cm (i.e. the value obtained after fitting the leaching curves of the tracer)

and the adsorption constants (Table 3), provides a poor description of the experimental results. A better match is obtained if the K_f value is taken as zero. Such a consideration, based on the low adsorption capacity of the soil ($K_f = 0.12 \text{ cm}^3 \text{ g}^{-1}$) and the rapid water-flow rate observed in this column, reveals that the adsorption constant calculated in the batch experiment does not agree with the adsorption of bentazone in this soil column.

The retardation factor for bentazone in the P_2 soil column was lower than unity (0.90). Such a low value can be explained by the anion exclusion process described above in the displacement of the tracer through this soil column. The average distance calculated for the displacement of bentazone (eqn (2)), 33.98 cm, shows that this herbicide flows out of the soil column. This result agrees with the mass balance carried out for the soil column, which also reveals the total elution of bentazone after irrigation with $22.87 \text{ cm}^3 \text{ cm}^{-2}$.

The experimental data obtained for the displacement of bentazone through the P_7 soil column were similar to those obtained with the chloride-ion tracer, in that a rapid displacement occurred, with bentazone appearing in the first eluates collected and a peak concentration being reached after 3 h of irrigation. The same explanation as we have suggested for the rapid elution of the tracer may also be used to explain the quicker elution of bentazone through this soil column in comparison with the P_2 column at the same water flow-rate. Given the high clay content and pH (7.7) of this soil, in which bentazone molecules should mostly be in the form of dissociated anions, anionic molecules may have emerged earlier in the P_2 soil column because of anion repulsion by the negatively charged clay particles. Thus, the water volume of irrigation to flowout of the anionic bentazone molecules may—as with the tracer—be considerably less than the total pore volume of the P_2 soil column. This phenomenon of anion repulsion seems to have been stronger in this soil than in the others alkaline soils, as a result of its higher clay content.

The results of the bentazone leaching simulation in the P_7 soil column show that—as in the P_2 soil column—the best match was achieved by the curve simulated with an adsorption value of zero ($K_f = 0$). However, in this clay soil, the experimental bentazone concentration at the peak of the curve was higher than the simulated one. This again may be due to the anion-repulsion process, causing negative adsorption of bentazone in this soil column.

In general, the best description of the model for bentazone displacement was obtained for the P_{10} soil column. The good match may be due to this column's slower water flow-rate and, hence, to the smaller differences between the adsorption constant calculated in the batch and column experiments. Furthermore, under such flow conditions, the anion repulsion and exclusion

processes may be less significant in the displacement of these anionic solutes.

The results of the bentazone leaching experiments in the P_{10} , P_7 and P_2 soil columns show that more than 88% of the herbicide applied will leach through the soil down the root zone. These results agree with those reported by other authors in column experiments under laboratory conditions with acidic soils and generally high organic matter content.² However, they differ from the results obtained under field conditions with lysimeter experiments,^{3–5} in which bentazone was present in the initial leachates—as in our results—but after 60 days less than 2% of the herbicide applied was recovered. This difference in behaviour may, as previous authors have suggested,³ perhaps be explained by a non-equilibrium in the adsorption of bentazone under laboratory conditions, owing to elution being quicker than under field conditions. It is also important to take differences in the temperature and humidity of the soil surface into account under field conditions. Thus, the dissipation of bentazone by other means such as photodegradation or volatilization should also be considered in the mass balance, especially if the half-life of bentazone on the soil surface is extremely short as a result of photodegradation.¹⁸

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